

Spin-lattice NMR relaxation by anomalous translational diffusion

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Abstract

A model-free theoretical framework for a phenomenological description of spin-lattice relaxation by anomalous translational diffusion in inhomogeneous systems based on the fractional diffusion equation is developed. The dependence of the spin-lattice relaxation time on the size of the pores in porous glass Vycor is experimentally obtained and found to agree well with our theoretical predictions. We obtain nonmonotonic behavior of the translational spin-lattice relaxation rate constant (it passes through a maximum) with the variation of the parameter referring to the extent of inhomogeneity of the system.

Key words:

spin-lattice relaxation, disordered systems, porous media, fractional diffusion equation.

PACS: 61.18.Fs, 61.43.Fs, 61.43.Gt

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1 Introduction

Anomalous diffusion processes in randomly disordered media are of considerable interest at present (see [1] and refs. therein). The list of examples includes, glasses and supercooled liquids [2], porous [3], [4], [5], percolative [6], [7], [8], polymeric [9] and diffusive [10] systems, etc. One of the powerful methods for investigation of such processes is that of nuclear magnetic resonance (NMR) diffusometry [3]. The latter was successfully applied to the systems listed above [3-9]. The theory of NMR diffusometry in disordered media [4], [8] is developed within the framework of a modern approach to anomalous diffusion [1] invoking the so called fractional calculus [11].

The aim of the present paper is to report the experimental results on spin-lattice relaxation time in porous glass Vycor with molecules of hexane as a diffusion tracer and to compare them with phenomenological generalization of the theory of spin-lattice relaxation in homogeneous media for the case of inhomogeneous one.

A modern description of anomalous diffusion processes in disordered (e.g., porous) media makes use of the so called fractional diffusion equation (FDE). The idea of this approach goes back to many pioneers whose achievements are honored in the review article [1]. The reason for introducing this equation is as follows. As is well known the mean squared displacement of a free particle in a homogeneous media increases linearly with time $\langle x^2(t) \rangle \sim C_1 t$ where C_1 is the diffusion coefficient with the dimension cm^2/s . This conventional Einstein relationship of the classical theory results from the ordinary diffusion

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equation for the probability density function to find the particle at position x at time t and is a direct consequence of the Fick's second law. In the case of an inhomogeneous media a disorder (like e.g., obstacles caused by walls of pores in a porous materials) leads to a slower increase of the mean squared displacement with time

$$\langle x^2(t) \rangle \sim C_\alpha t^\alpha \quad (1)$$

where C_α is the diffusion coefficient with the dimension cm^2/s^α and $0 < \alpha \leq 1$ is a phenomenological parameter characterizing the extent of inhomogeneity. Such behavior is called sub-diffusion and it originates in any fractal media due to the presence of dead ends on current ways. It should be stressed that the departure from the classical theory is of fundamental character and the latter relationship can not be reduced to the former one by simple scaling of time and diffusion coefficient. The most straightforward way to obtain mathematically sub-diffusion is to generalize the ordinary diffusion equation by replacing the ordinary derivative in time by the fractional one of the order α . The resulting FDE is a convenient mathematical tool although a phenomenological one since there is no lucid and commonly accepted physical meaning of a fractional derivative at present. Some theoretical motivation for introducing the FDE arises from its intrinsic relationship with the so called continuous time random walk theory. In fact the FDE can be derived from a generalized Langevin equation with the memory kernel accounting for a power-law waiting time statistics of the trapping events [1].

Much work is being carried out at present to verify experimentally the predictions of the approach based on the FDE [4], [8], [10]. As is emphasized in the papers [4], [8] NMR microscopy enabled the authors to verify the anomalous

solutions of the FDE for the first time. The results of these work are compatible with other approaches to NMR relaxation in porous media [28],[29]. However the fact that the authors of [4], [8] resort to a one-dimensional fractional counterpart of the ordinary diffusion equation makes their theoretical calculations essentially of qualitative character and leaves room for further advances. The present paper is a development along this line. We resort to a three-dimensional FDE and obtain stringent quantitative relationship of the spin-lattice relaxation rate constant with the parameters (α and C_α) of the FDE. Our results provide new and useful analytical tool to interpret the manifestation of anomalous translational diffusion in NMR relaxation which is substantiated by the obtained experimental data.

The matter of NMR relaxation at diffusion through a pore is of particular significance for biological systems. According to a widely accepted point of view one of the ways of molecule penetration through a biological membrane is associated with the short-lived and long-lived pores with a diameter of several Engströms [12]. Such pores are identified with proteins - aquaporins revealed in cellular membranes of various organisms [13], [14]. In that case the water molecules can move only one by one according to the so called single file diffusion. Such pores seem to be mostly suitable for providing selection and thin regulation of the transfer but the question about their reality and peculiarities of their functioning still remains a matter of discussion.

At present the dynamics of molecules of liquids in porous systems attracts considerable attention with an accent on the questions of multi-dimensionality of the diffusion and the existence of bound motion [15], [16]. The diffusion of water in pores with a diameter comparable with that of water molecules is studied by molecular dynamics [17-20]. In [18] it is shown that fluid mechan-

ics (classical hydrodynamics) can be qualitatively extrapolated for the one by one motion of the water molecules in pores with the diameter of 3 Engströms. Water in a narrow pore retains the properties of liquid state with the diffusion coefficient of approximately 70% of that in the bulk phase. In [19], [20] it is shown that water in narrow pores has the properties of a structured liquid with angular and radial distributions and with the diffusion coefficient comparable with that of the bulk phase. According to the data of neutron diffraction spectroscopy the characteristic time of passing of the water molecule through the membrane is of order of 100 mks [21] and thus finds itself within the time scale of the processes amenable to NMR spectroscopy. It is reasonable to expect that the constraint of the water molecules' motion and their interaction with the walls of the pores leads to peculiarities of magnetic relaxation of water. Our final interest in transport processes in biological membranes motivates the present attempt to consider magnetic relaxation by translational diffusion in the pores of much simpler object namely a porous glass.

Concluding the Introduction we would like to emphasize the following fact. The FDE is much more adequate than the ordinary diffusion equation for the description of processes in inhomogeneous media but one has to pay a hard cost for gained facilities. Namely the diffusion coefficient in the FDE acquires a functional dependence on the phenomenological parameter α referring to the extent of inhomogeneity. This dependence is not known in general case and at present one can only guess some trial possibilities for particular systems of interest. Besides this diffusion coefficient acquires the unusual dimension cm^2/s^α and thus has minimal crossing (only at $\alpha = 1$) with the ordinary diffusion coefficient with the dimension cm^2/s which can be obtained by direct measurements employing the existing scheme of Pulsed-Field Gradient NMR.

2 Results

2.1 Theory

The theory of spin-lattice relaxation by dipole-dipole interaction initiated by Bloembergen, Purcell and Pound and developed by Torrey and Abragam is presented in [22]. The rate constant of spin-lattice relaxation $1/T_1$ is decomposed into translational and rotational parts

$$1/T_1 = (1/T_1)_{trans} + (1/T_1)_{rot} \quad (2)$$

To calculate this value theoretically one needs to know the spectral density of the correlation function for spherical harmonics. The relationship of the value of the spectral density at a Larmor frequency ω_L with the value of the contribution to the spin-lattice relaxation rate constant due to translational diffusion is of the form

$$(1/T_1)_{trans} = \frac{3\gamma^4\hbar^2 I(I+1)}{2} \{J^{(1)}(\omega_L) + J^{(2)}(2\omega_L)\} \quad (3)$$

where γ is the gyromagnetic ratio of the nucleus, I is their spin and \hbar is the Planck constant. The spectral densities are proportional to the function $J(\omega)$ of the spectral density: $J^{(1)}(\omega) = \frac{8\pi}{15}J(\omega)$ and $J^{(2)}(\omega) = \frac{32\pi}{15}J(\omega)$. Thus one actually needs to calculate the only function $J(\omega)$. The consideration of the spin-lattice relaxation in homogeneous media due to diffusion motion of the particles presented in [22] is based on the ordinary diffusion equation for the probability density.

How is the value of $1/T_1$ altered when we pass from a homogeneous system to a disordered (e.g., porous) one ? One can expect that $(1/T_1)_{trans}$ is very sensitive to the extent of porosity in the whole range while $(1/T_1)_{rot}$ becomes to feel the porosity only when the size of the pores becomes commensurate with that of the molecules, i.e. in a wide range of porosity it remains constant. That is why namely the dependence of the value $(1/T_1)_{trans}$ on the extent of porosity is of interest for theoretical consideration in the present paper. We develop the latter within the framework of a modern approach to anomalous translational diffusion in disordered systems based on the FDE. The reason to resort to such generalization of the ordinary diffusion equation for the description of anomalous diffusion processes is stated in the Introduction.

The generalization of the ordinary diffusion equation within the fractional calculus was suggested by Schneider and Wyss [23]

$$\frac{\partial P(\bar{r}, t)}{\partial t} = C_\alpha (D_{0+}^{1-\alpha} \nabla^2 P)(\bar{r}, t) \quad (4)$$

where $P(\bar{r}, t)$ is the probability density function to find the particle at position \bar{r} at time t , ∇^2 is the three-dimensional Laplace operator, C_α denotes the fractional diffusion constant with the dimension $[\text{cm}^2/\text{s}^\alpha]$ and $D_{0+}^{1-\alpha}$ is the Riemann-Liouville fractional derivative of order $1-\alpha$ and with lower limit $0+$ which is defined via the following relationship [11]

$$(D_{0+}^{1-\alpha} f)(x) = \frac{1}{\Gamma(\alpha)} \frac{d}{dx} \int_0^x (x-y)^{\alpha-1} f(y) dy \quad (5)$$

where $\Gamma(x)$ is a gamma function. The solution of equation (4) for the case of sub-diffusion $0 < \alpha \leq 1$ with the initial condition $P(\bar{r}, 0) = \delta(\bar{r})$ where $\delta(x)$ is a Dirac function is obtained in [23] and expressed via the Fox's function

[24],[25],[26]

$$P(\bar{r}, t) = \frac{1}{(r^2\pi)^{3/2}} H_{12}^{20} \left(\frac{r^2}{4C_\alpha t^\alpha} \left| \begin{array}{c} (1, \alpha) \\ (3/2, 1), (1, 1) \end{array} \right. \right) \quad (6)$$

The latter is defined as $H_{pq}^{mn} \left(z \left| \begin{array}{c} (a_1, A_1), \dots, (a_p, A_p) \\ (b_1, B_1), \dots, (b_p, B_p) \end{array} \right. \right) = \frac{1}{2\pi i} \int_L ds z^{-s} \eta(s)$

where $\eta(s) = \frac{\prod_{i=1}^m \Gamma(b_i + B_i s) \prod_{i=1}^n \Gamma(1 - a_i - A_i s)}{\prod_{i=n+1}^p \Gamma(a_i + A_i s) \prod_{i=m+1}^q \Gamma(1 - b_i - B_i s)}$. The nomenclature in the Fox's function associated with the vertical bar is explained via its explicit definition by the contour integral. The requirements to the contour path L are formulated in [24].

Now we follow the algorithm of [22] (in what follows all corresponding results from [22] are obtained as a particular case $\alpha=1$ of the present approach). Under \bar{r} we denote the vector $\bar{r}_1 - \bar{r}_2$ connecting two identical molecules diffusing relative to each other rather than the radius-vector of the molecule diffusing relative to a fixed point. This leads only to the change of $4C_\alpha t^\alpha$ by $8C_\alpha t^\alpha$ in (6). Our aim is to calculate the correlation function

$$G(t) = N \iint \frac{\Upsilon_2^{m*}(\theta(0), \varphi(0))}{r_0^3} \frac{\Upsilon_2^m(\theta(t), \varphi(t))}{r^3} P(\bar{r} - \bar{r}_0, t) d^3 r_0 d^3 r \quad (7)$$

where N is the number of spins in 1 cm^3 , $\Upsilon_n^m(\theta, \varphi)$ is a spherical harmonic and $*$ denotes complex conjugate. To be more precise we need the spectral density of the correlation function $G(t)$ to calculate the spin-lattice relaxation rate constant with the help of (2). At integration in (7) one should take into account that r and r_0 can not be less than some limit value d – the least distance to which the molecules can approach to each other. If the molecules

are considered as spheres of the radius a then $d = 2a$ [22].

Making the Fourier transforming of the function $P(\bar{r} - \bar{r}_0, t)$ with the mentioned above change of $4C_\alpha t^\alpha$ by $8C_\alpha t^\alpha$ and literally repeating the manipulation of [22] with spherical functions one obtains

$$G(t) = \frac{4N}{\pi^{1/2}d^2} \int_0^\infty \frac{du}{u^2} \left[J_{\frac{3}{2}}(u) \right]^2 \int_0^\infty \frac{dR}{R^2} \sin\left(\frac{uR}{d}\right) \times$$

$$H_{12}^{20} \left(\frac{R^2}{8C_\alpha t^\alpha} \left| \begin{array}{c} (1, \alpha) \\ (3/2, 1), (1, 1) \end{array} \right. \right) \quad (8)$$

where $J_\nu(x)$ is a Bessel function of order ν and $R = |\bar{r} - \bar{r}_0|$. The integration can be fulfilled and yields the expressions for both the correlation function and its spectral density via Fox's functions. However a Fox's function is to regret not tabulated at present either in *Mathematica* or *Maple* or *Matlab*. Thus it is rather difficult to use such formulas for plotting the behavior of the correlation function and the spectral density. That is why it is useful to obtain another representation of the spectral density which enables one to plot the frequency dependence of this function. For this purpose we make the Fourier transforming of the Fox function in (8). The latter can be achieved with the help of the following trick going back to original investigations of Fox. In [23] the Mellin transform of the Fox function is given

$$M \left\{ H_{12}^{20} \left(\frac{r^2}{8C_\alpha t^\alpha} \left| \begin{array}{c} (1, \alpha) \\ (3/2, 1), (1, 1) \end{array} \right. \right) \right\} (s) =$$

$$\frac{1}{\alpha} \left(\frac{r}{(8C_\alpha)^{1/2}} \right)^{\frac{2s}{\alpha}} \Gamma\left(\frac{3}{2} - \frac{s}{\alpha}\right) \frac{\Gamma(1 - s/\alpha)}{\Gamma(1 - s)} \quad (9)$$

Now we make use of the identity [27]

$$F_C \{f(x); \omega\} = M^{-1} \left\{ \Gamma(s) \cos \frac{\pi s}{2} M \{f(x); 1-s\} \right\} \quad (10)$$

where F_C denotes the cosine Fourier transform and M denotes the Mellin transform which for our case is given by formula (9). We denote the characteristic time

$$\tau_\alpha = \left(\frac{d^2}{2C_\alpha} \right)^{1/\alpha} \quad (11)$$

As a result we obtain

$$J(\omega) = \frac{N\tau_\alpha^{1-\alpha}}{C_\alpha d (\omega\tau_\alpha)^{1-\alpha}} \sin \frac{\pi\alpha}{2} \int_0^\infty du \left[J_{\frac{3}{2}}(u) \right]^2 \times \frac{u}{u^4 + (\omega\tau_\alpha)^{2\alpha} + 2u^2 (\omega\tau_\alpha)^\alpha \cos \frac{\pi\alpha}{2}} \quad (12)$$

The integral in (12) can be easily calculated numerically. We use *Mathematica* for this purpose. Formula (12) is the main theoretical result of the present paper. This formula is a direct generalization of the textbook result (see e.g., [22] formula VIII.114) for the homogeneous case $\alpha = 1$ for the case of arbitrary $0 < \alpha \leq 1$. The spectral density is finite at $\omega\tau_\alpha \rightarrow 0$ only for $\alpha=1$. At all $\alpha < 1$ it is power-law divergent in this limit.

2.2 Phenomenology

The predictions of the present theory are defined by the dependence of the diffusion coefficient C_α on the phenomenological model parameter α referring to the extent of inhomogeneity. This dependence is of most interest because it characterizes the disordered media [1], [8], [10]. Its derivation is a separate and

still open problem. It should be a matter of a fundamental theory and is out of the scope of the present paper. In our phenomenological approach we restrict ourselves by a model example. As such we choose a particular behavior of the diffusion coefficient

$$C_\alpha = \frac{d^2}{2\Gamma(\alpha)} \left(\frac{2C_1}{d^2} \right)^\alpha \quad (13)$$

where C_1 is given by the Stokes formula

$$C_1 = \frac{k_B T}{6\pi a \eta} \quad (14)$$

Thus the characteristic time is parameterized as

$$\tau_\alpha = \tau_1 \Gamma(\alpha)^{1/\alpha} \quad (15)$$

where

$$\tau_1 = \frac{12\pi a^3 \eta}{k_B T} \quad (16)$$

The behavior of the spectral density at several values of the parameter α is depicted in Fig.1. Substitution of (12),(13) and (15) into (3) yields the normalized spin-lattice relaxation rate constant

$$\begin{aligned} & \frac{5dC_1}{4\pi N \gamma^4 \hbar^2 I(I+1)} (1/T_1)_{trans}(\omega_L) = \\ & (\omega_L \tau_1)^{\alpha-1} \Gamma(\alpha) \sin \frac{\pi\alpha}{2} \int_0^\infty du \left[J_{\frac{3}{2}}(u) \right]^2 u \times \\ & \left\{ \frac{1}{u^4 + (\omega_L \tau_1)^{2\alpha} \Gamma(\alpha)^2 + 2u^2 (\omega_L \tau_1)^\alpha \Gamma(\alpha) \cos \frac{\pi\alpha}{2}} + \right. \\ & \left. \frac{2^{\alpha+1}}{u^4 + (2\omega_L \tau_1)^{2\alpha} \Gamma(\alpha)^2 + 2u^2 (2\omega_L \tau_1)^\alpha \Gamma(\alpha) \cos \frac{\pi\alpha}{2}} \right\} \quad (17) \end{aligned}$$

Its behavior on the parameter of inhomogeneity α at different values of $\omega_L\tau_1$ is depicted in Fig.2. At experimentally used Larmor frequency $\omega_L\tau_1 \approx 0.015$ the rate constant of spin-lattice relaxation has a maximum at $\alpha \approx 0.35$ (with $\omega_L\tau_\alpha \approx 0.21$).

2.3 Objects of investigation, experimental procedure and results

Porous glasses of the class "Vycor", with characteristics presented in Table 1, were used as model samples of porous media. There R is the size of glass microparticles, p is the pore radius, S_n and V_n are the pore specific surface area and volume, respectively. The primary porosity of these glasses is determined by the pore size p , and the secondary one is determined by the glass microparticle size R .

In the experiment, hexane vapor was absorbed at the temperature of 21°C in the Π -shaped cell consisting of two connected tubes with the inner diameter of 7 mm. One tube was filled with a sample of porous glass to the height of 12 mm, and into the other tube the liquid hexane was poured. Hexane vapor absorption took place in the presence of a certain amount of air. Prior to cell soldering, the leg with porous glass was heated at the temperature of 140°C to remove water vapor. The amount of the absorbed hexane was determined from the amplitude of free induction decay after the 90° radio frequency pulse. The calibrating of the signal was carried out using the reference sample with the known contents of protons. The process of absorption consists of two stages. The first faster stage has the character of mono molecular absorption and is terminated at the amount of absorbed molecules equal or close to the amount necessary to form a mono molecular layer. The second slow stage is

associated with the capillary condensation, and lasts from 24 hours ("Vycor 20") to a month and a half ("Vycor 200"), and is accomplished by filling the micropores. A good coincidence of calculated and measured values of the amount of hexane, necessary to fill completely the primary pores, is observed. Spin-lattice relaxation times, T_1 , of absorbed hexane were measured using a zero-method of the pulse sequence $180^\circ - 90^\circ$ on the coherent NMR relaxation meter using protons at the frequency of 19.5 MHz. Taking the average size of a hexane molecule as $a = 5\text{\AA}$ ($d = 2a = 10\text{\AA}$) and its diffusion coefficient in bulk water as $4.17 * 10^{-5} \text{cm}^2/\text{s}$ at room temperature we obtain $\tau_1 \approx 10^{-10} \text{s}$ and consequently $\omega_L \tau_1 \approx 0.015$.

The decay of the longitudinal magnetization of the hexane in the region of full filling of the pores is one-exponential for all porous glasses. As an example the decay of the longitudinal magnetization of the hexane in the "Vycor 160" is presented in Fig.3. The experimentally observed spin-lattice relaxation times depending on the inverse radius of the pores are plotted in Fig.4. One can see that with the variation of the pore size from 400 \AA to 55 \AA the rate of longitudinal relaxation increases and for $p=20$ \AA it begins to decrease in accordance with the prediction of the theory.

3 Discussion

Our theoretical approach is based on the FDE like that of the papers [4], [8]. However in these papers a one-dimensional fractional counterpart of the ordinary diffusion equation is employed to gain qualitative insight. In contrast we consider a three-dimensional one that enables us to develop quantitative formalism. In our approach we do not a priory assume any type and character of

the motion like e.g., quasi-two-dimensional bulk mediated surface diffusion of the absorbed molecules in the pores [4]. Our approach due to its phenomenological model-free character is flexible enough to include formally such type of motion as a particular case.

Translational diffusion was previously taken into account within the so called reorientation mediated by translational displacements model [3], [4]. It is assumed there that dipolar coupling responsible for the relaxation mechanism is predominantly of an intramolecular nature, i.e. the fluctuations causing relaxation are exclusively due to molecular reorientations [3]. In our approach we emphasize another facet of translational diffusion manifesting itself in the intermolecular interactions. We conceive the process as a bulk three-dimensional diffusion in space with obstacles imposed by the porous media. In our opinion the porosity of any extent considerably manifests itself in the translational diffusion. On the other hand it can affect rotational diffusion appreciably only when the size of pores becomes commensurate with that of the molecules. That is why the value of $(T_1)_{rot}$ is independent on the size of the pores in a wide range of the extent of porosity while $(T_1)_{trans}$ is very sensitive to this parameter. The latter value characterizes the porosity of the system and is of main interest in the present paper.

The most important feature of the spectral density (12) which distinguishes it in the general case from the particular one $\alpha = 1$ considered in [22] is the divergence of the spectral density at low frequencies (see Fig.1). Our phenomenological model-free approach can be compared with that based on a molecular model of the porous system [28]. Fig.1 is qualitatively similar to Fig.2 from [28]. However there are significant quantitative distinctions between two approaches. The authors of [28] obtain a logarithmic divergence of

the spectral density at low frequencies while we obtain a power-law one. Our result agrees with the conclusions of the papers [4], [29] where a power-law divergence $1/T_1 \propto 1/\omega^\beta$ at low frequencies is reported. However the authors of these papers conclude that the proton relaxation process is mainly due to intramolecular dipolar interaction while we explore the range of inhomogeneity (particularly porosity) of the system where in our opinion intermolecular interactions of molecules determine the dependence of the relaxation rate constant on translational diffusion process.

It is known that a confinement enhances significantly both spin-lattice and spin-spin relaxation rate constants and alters their frequency and temperature dependencies (see [28] and refs. to previous works of its authors). In these papers a monotonic behavior of the spin-lattice relaxation rate constant ($1/T_1 \propto 1/p$ or $1/T_1 \propto 1/p^2$ where p is the average pore size) is reported. In contrast we obtain nonmonotonic behavior of the translational spin-lattice relaxation time with the variation of the parameter α referring to the extent of inhomogeneity (or that of porosity, namely the size of the pores) with $\alpha = 1$ corresponding to the case of homogeneous system. We find that at a given temperature there is an optimal porosity for maximal spin-lattice relaxation rate constant. Such behavior is determined by contribution from translational diffusion. For experimentally used Larmor frequency $w_L\tau_1 \approx 0.01$ and for a particular model dependence of the fractional diffusion coefficient on the parameter of inhomogeneity the rate constant of relaxation first increases with the decrease of α then passes through a maximum at $w_L\tau_\alpha \approx 0.1$ and finally sharply decreases. The reason for such behavior is quite similar to that for ordinary diffusion in a homogeneous system with the variation of temperature. In the latter case the characteristic time $\tau_1(T)$ is a function of temperature

and the rate constant of spin-lattice relaxation has a maximum at some temperature where $\omega_L\tau_1 \approx 1$. For inhomogeneous systems the characteristic time $\tau_\alpha(T, \alpha)$ besides temperature is a function of the parameter of inhomogeneity α and the variation of the latter (e.g., that of the porosity of the system) at constant temperature leads to a maximum of the spin-lattice relaxation rate constant at some α . However this maximum in general case exists at $\omega_L\tau_\alpha$ different from 1.

4 Conclusions

A generalization of the ordinary diffusion equation within the framework of the fractional calculus provides natural phenomenological generalization of the theory of spin-lattice NMR relaxation in homogeneous systems for the case of the inhomogeneous ones. This development is carried out within a general modern trend to extend the theory of Gaussian translational diffusion in homogeneous systems for the case of anomalous diffusion in disordered (e.g., porous) systems by making use of the fractional diffusion equation. The translational contribution into spin-lattice relaxation time is found to be highly sensitive to the extent of inhomogeneity. It exhibits nonmonotonic behavior with the variation of the parameter α referring to the extent of inhomogeneity (with $\alpha = 1$ corresponding to the case of a homogeneous and isotropic system and $\alpha = 0$ corresponding to that of an absolutely inhomogeneous one). The rate constant of relaxation passes through a maximum with the decrease of α . For experimentally used Larmor frequency $\omega_L\tau_1 \approx 0.015$ and for a particular model dependence of the fractional diffusion coefficient on the parameter of inhomogeneity the maximum is at $\alpha \approx 0.35$ ($\omega_L\tau_\alpha \approx 0.21$). One can conclude

that the present work provides a reliable theoretical framework for the analysis of anomalous translational diffusion processes by NMR microscopy.

We obtain the explicit dependence of the rate constant of spin-lattice relaxation by anomalous translational diffusion on the parameter of inhomogeneity α taking place in the fractional diffusion equation. Formula (12) is a direct generalization of the textbook result (see e.g. formula VIII.114 in [22]) for the homogeneous case $\alpha = 1$ for the case of arbitrary $0 < \alpha \leq 1$. Our calculations predict that there occur a maximum of the relaxation rate constant at varying this parameter. We carry out experimental measurements of the relaxation rate constant in porous glass Vycor and obtain data which agree well with our theoretical findings.

Acknowledgements. The authors are grateful to Prof. V.D. Fedotov and R.Kh. Kurbanov for helpful discussions. The work was supported by the grant from RFBR.

References

- [1] R. Metzler, J. Klafter, The random walk's guide to anomalous diffusion: a fractional dynamics approach, Phys. Rep. 339 (2000) 1-77.
- [2] Götze, L. Sjögren, Relaxation process in supercooled liquids, Rep. Prog. Phys. 55 (1992) 241-376.
- [3] R. Kimmich, NMR: Tomography, Diffusometry, Relaxometry, Springer, Berlin, 1997.
- [4] R. Kimmich, Strange kinetics, porous media, and NMR, Chem.Phys. 284 (2002)

253-285.

- [5] A.L. Dullien, Porous Media: Fluid Transport and Pore Structure, Academic Press, New York, 1992.
- [6] A. Klemm, H.-P. Müller, R. Kimmich, NMR microscopy of pore-space backbones in rock, sponge, and sand in comparison with random percolation model objects, Phys.Rev. E 55 (1997) 4413-4422.
- [7] A. Klemm, H.-P. Müller, R. Kimmich, Evaluation of fractal parameters of percolation model objects and natural porous media by means of NMR microscopy, Physica 266A (1999) 242-246.
- [8] A. Klemm, R. Metzler and R. Kimmich, Diffusion on random percolation clusters. Theory and NMR microscopy experiments with model objects, Phys.Rev. E65 (2002) 021112.
- [9] E. Fischer, R. Kimmich, N. Fatkullin, NMR field gradient diffusometry of segment displacements in melts of entangled polymers, J. Chem. Phys. 104 (1996) 9174-9178.
- [10] T. Kosztolowicz, K. Dworecki, and St. Mrówczyński, Measuring subdiffusion parameters, Preprint arXiv:cond-mat/0309072.
- [11] K.B. Oldham, J. Spanier, The fractional calculus, Academic Press, New York, 1974.
- [12] A.K. Solomon, Characterization of biologic membranes by equivalent pores, J. Gen. Physiol. 51 (1968) 335-347.
- [13] J.S. Jung, G.M. Preston, B.L. Smith, W.B. Guggino, P. Agre, Molecular Structure of the Water Channel Through Aquaporin CHIP. The Hourglass Model, J.Biol.Chem. 269 (1994) 14648-14654.

- [14] S.D. Tyerman, H.J. Bohnert, C. Maurel, E. Steudle, J.A.C. Smith, Plant Aquaporin: Their Molecular Biology, Biophysics and Significance for Plant Water Relations, *J.Exp.Bot.* 50 (1999) 1055-1071.
- [15] K.J. Packer, F.O. Zelaya, Observations of diffusion of fluids in porous solids by pulsed field gradient NMR, *Coll. Surf.*, 36 (1989) 221-227.
- [16] P.T. Callaghan, Pulsed field gradient NMR as a probe of liquid state molecular organization, *Austr. J. Phys.*, 37 (1984) 359-387.
- [17] D.G. Levitt, Dynamics of a single-file pore: non-Fickian behavior, *Phys. Rev.*, A8 (1973) 3050-3054.
- [18] D.G. Levitt, Kinetics of diffusion and convection in 3.2 Å pores. Exact solution by Computer stimulation, *Biophys. J.*, 13 (1973) 186-206.
- [19] S.K. Aityan, Single-file transport of incharged particles, *Gen. Physiol. Biophys.*, 4 (1985) 3-14.
- [20] S.K. Aityan, Y.A. Chizmadzhev, Simulation of molecular dynamics of water movement in ion channels, *Gen. Physiol. Biophys.*, 5 (1986) 213-229.
- [21] N.P. Franks, W.R. Lieb, Rapid movement of molecules across membranes. Measurement of the permeability coefficient of water using neutron diffraction, *J. Mol. Biol.* 141 (1980) 43-61.
- [22] A. Abragam, Principles of nuclear magnetism, Clarendon Press, Oxford, 1961.
- [23] W. Schneider, W. Wyss, Fractional diffusion and wave equations, *J. Math. Phys.* 30 (1989) 134-144.
- [24] H. Srivastava, K. Gupta and S. Goyal, The H-function one and two variables with applications, South Asian Publishers, New Delhi, 1982.
- [25] A.P. Prudnikov, Yu.A. Brychkov, O.I. Marichev, Integrals and series. Additional chapters, Nauka, Moscow, 1986.

- [26] W.G. Glöckle, T. Nonnenmacher, Fox function representation of non-Debye relaxation processes, *J. Stat. Phys.* 71 (1993) 741-757.
- [27] H. Schiessel, R. Metzler, A. Blumen and T.F. Nonnenmacher, Generalized viscoelastic models: their fractional equations with solutions, *J. Phys. A: Math. Gen.* 28 (1995) 6567-6584.
- [28] J.P. Korb, S. Hu, J. Jonas, Confinement effects on dipolar relaxation by translational dynamics of liquids in porous silica glasses, *J. Chem. Phys.* 98 (1993) 2411-2422.
- [29] P. Levitz, J.P. Korb, D. Petit, Slow dynamics of embedded fluid in mesoscopic confining systems as probed by NMR relaxometry, *Eur. Phys. J. E* 12 (2003) 2933.

Table 1

Characteristics of porous glasses.

Designations	R , mm	p , \AA $\pm 10\%$	S_n , m^2/g $\pm 5\%$	V_n , cm^2/g $\pm 5\%$
Vycor 20	0.1 – 0.3	20	200	0.2
Vycor 55	<0.05	55	254	0.7
Vycor 160	0.1 – 0.2	160	137.5	1.1
Vycor 220	0.1 – 0.3	220	118	1.3
Vycor 400	<0.1	400	25	0.5

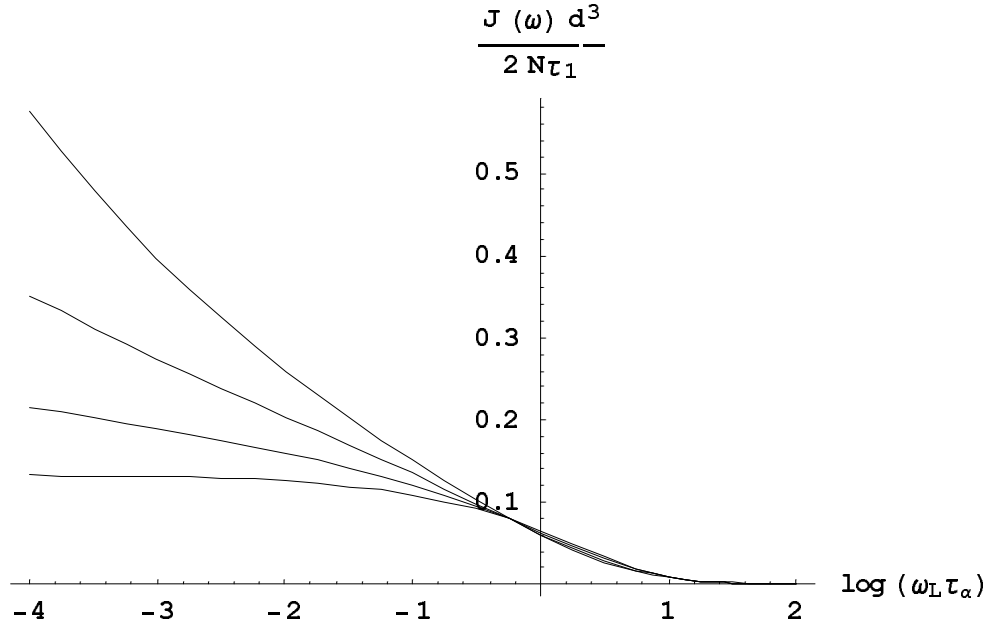


Fig. 1. The dependence of the spectral density of the correlation function for spherical harmonics due to anomalous translational diffusion given by the (12) on the reduced Larmor frequency $\omega_L \tau_\alpha$ at different values of the parameter of inhomogeneity α . The values of the latter parameter from the down line to the upper one respectively are: 1; 0.95; 0.9; 0.85. Here N is the number of spins in 1 cm^3 , d is the doubled radius of the molecules, τ_1 is the characteristic time for the homogeneous media given by the (16) and τ_α is the characteristic time for the inhomogeneous media given by the (15).

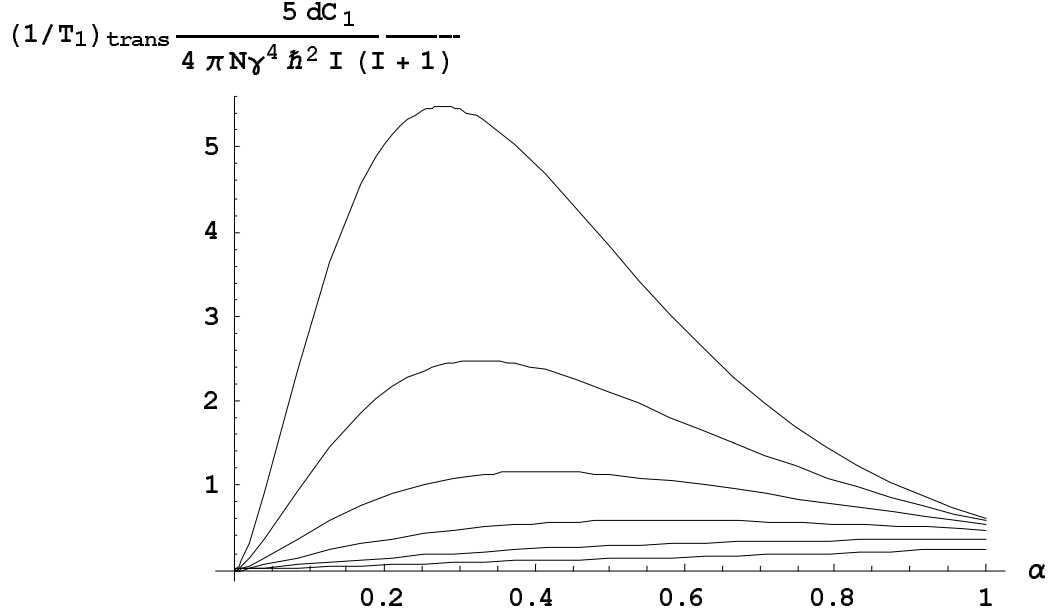


Fig. 2. The dependence of the contribution to the spin-lattice relaxation rate constant due to anomalous translational diffusion given by the (17) on the parameter of inhomogeneity α at different values of the reduced Larmor frequency $\omega_L \tau_1$. The values of the latter parameter from the down line to the upper one respectively are: 1.; 0.4; 0.16; 0.06; 0.025; 0.01. Here N is the number of spins in 1 cm^3 , d is the doubled radius of the molecules, C_1 is the diffusion coefficient for the homogeneous media given by the Stokes formula (14), τ_1 is the characteristic time for the homogeneous media given by the (16), γ is the gyromagnetic ratio of the nucleus, I is their spin and \hbar is the Planck constant.

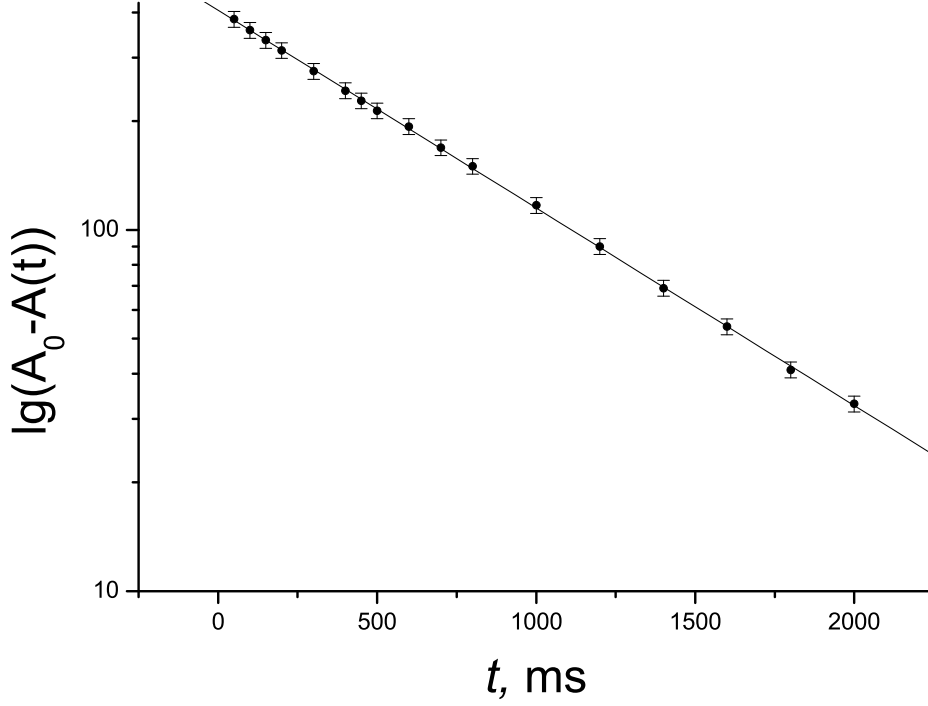


Fig. 3. The experimental decay of the longitudinal magnetization for hexane in the porous glass Vycor 160 with the radius of the pores 160 Å. Solid line is the result of the linear fit of the data. Here t is the current time of the magnetization's relaxation, A_0 is the equilibrium value of the magnetization and $A(t)$ is the current value of the magnetization.

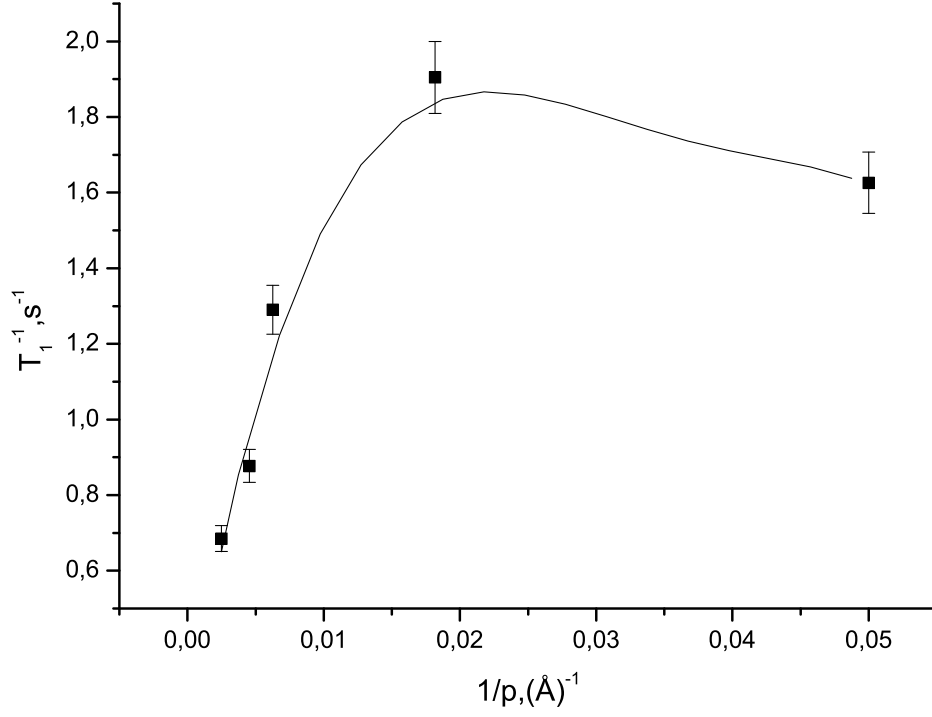


Fig. 4. The experimental dependence of the spin-lattice relaxation rate constant on the reciprocal radius of the pores for the porous glasses Vycor at the Larmor frequency 19.5 MHz. Here T_1 is the spin-lattice relaxation time and p is the radius of the pores measured in Engströms \AA . The solid line is an empirical fitted one "to guide the eye".